

STYRENE-DIVINYLBENZENE POLYMER OXIDATION CATALYST

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Some additional data about properties and applicability of a styrene-divinylbenzene polymer catalyst containing acidic and redox functional groups are reported. It is shown that the catalysts of this type can be prepared reproducibly and exhibit catalytic properties comparable to the properties of noble metal catalysts.

In previous works¹⁻³ we studied the redox capacity and oxidation catalytic activity of styrene-divinylbenzene copolymers containing several types of catalytically active groups attached to the macromolecular skeleton. These were quinone or hydroquinone groups, sulphonic acid groups and species not precisely identified, the structure of which can be depicted by polycondensated aromatic rings up to the clusters of carbon atoms. With regard to the fact that their catalytic oxidation activity depended strongly on the presence of acidic sulphonic acid groups, one can assume that the oxidation process is closely related to the acid-base interaction of reactants with the acidic groups on the polymer surface.

The first of the above mentioned works concerned especially with the synthesis of catalysts which was based on the substitution of the catalytically inactive support by catalytically active quinone and sulphonic acid groups. The results showed, however, that chemical reactions used to introduce functional groups into the polymer induce also a number of defects in the styrene-divinylbenzene copolymer, some of which have redox properties. For that reason, the attempt was further made to find such a procedure for preparing polymer oxidation catalysts in which the uniform functional groups and polymer structure have not been strictly required, the principal aim being the achievement of the highest catalytic activity. This approach had met with success and the best catalyst reported in the previous work³ equaled in its catalytic activity to the oxidation catalysts containing noble metals (Pt, Rh, Ir).

In the present work we report some additional data on the properties of oxidation catalysts of the above type with the aim to extend the knowledge of their properties and applicability.

EXPERIMENTAL

Starting compounds, experimental apparatus, procedure and analytical methods were the same as in our previous works¹⁻³.

Measurements of oxygen sorption were carried out in a vacuum apparatus, the pressure being determined with Rosemount, type 1332, pressure detecting element with the accuracy of ± 0.02 per cent. After the sorption vessel containing the known amount of the catalyst had been connected to the apparatus, the desorption was carried out at 120°C and $1.2 \cdot 10^{-3}$ Pa for 6 h.

The same temperature was also used to calibrate the empty volume of the flask by argon. Then the gas was again pumped off up to the pressure $1.3 \cdot 10^{-3}$ Pa, and the oxygen sorption was performed.

RESULTS AND DISCUSSION

The attention was first paid to a more detailed examination of conditions for preparing the oxidation catalysts from macroporous styrene-divinylbenzene chloromethylated copolymer containing 10% of divinylbenzene (catalyst A), eventually from the same polymer which was condensed with hydroquinone under conditions reported by Kun⁴ prior to further treatment (catalyst B). Both starting materials were used to synthesize several samples of catalysts *via* their sulphonation with concentrated sulphuric acid at 180°C for 6 h (ref.³). Individual samples differed from each other by the amount of the starting polymer so treated, this being used from 10 to 100 g. All the samples of the catalysts were characterized by the parameters presented in Tables I and III of our previous work³. It was found that for all the catalysts A and B obtained in this way, the values of these parameters differ from the catalysts of the same type which were prepared and tested earlier³ within ± 5 per cent. Only EPR signals showed greater fluctuations, similarly as in the previous case. It can be therefore stated that the methods used to prepare polymer oxidation catalysts and based on the sulphonation of the above polymers by concentrated sulphuric acid at 180°C for 6 h are reproducible under laboratory conditions.

In the first stage of the sulphonation, which takes several minutes, essentially all the chlorine is cleaved from the starting polymer as hydrogen chloride and in the course of the process, the part of sulphuric acid is reduced into SO₂ which is another gaseous product of the reaction. This indicates that SO₃ formed during the sulphonation of the copolymers creates the strongly oxidizing medium, which certainly affects the styrene-divinylbenzene copolymer. We have therefore determined the content of carboxylic groups, using titration method reported by Boyd and Soldano⁵. The obtained results are presented in Table I, along with the other properties of studied catalysts. The content of carboxylic groups is very high, essentially as high as is the content of sulphonic acid groups. However, with respect to their weak acidity, the presence of these functional groups has not effect on the course of the oxidation of 2-propanol as well as on its dehydration.

As one of the catalytically active functional groups of the catalysts under study is quinone group, we have compared the course of the oxidation of 2-propanol catalysed with the polymer containing quinone and sulphonic acid groups (catalyst H, Table I, ref.¹) with the oxidation catalysed by quinone dissolved in the reaction medium containing *p*-toluenesulphonic acid. Experiments were carried out under conditions identical with those used for the oxidation catalysed by the heterogeneous

catalyst in the liquid phase; the results are summarized in Fig. 1. They show that the heterogeneous catalyst is more active than quinone in homogeneous medium. The analysis of the reaction product showed that quinone reacts with the present *p*-toluenesulphonic acid to give a substance of higher molecular mass. As the oxidation of 2-propanol takes place also after all the quinone had disappeared from the reac-

TABLE I
Properties of prepared polymer oxidation catalysts

Property	Catalyst ^a	
	A	B
Titration exchange capacity, mequiv. H ⁺ /g	1.74	1.90
Titration redox capacity, mequiv. H/g	1.56	2.61
EPR signal, dB	9.8 · 10 ⁴	13.9 · 10 ⁴
Chlorine content, w. %	0.41	0.33
Sulphur content, w. %	8.51	8.82
Specific surface, m ² /g	24	27
Content of carboxylic groups, mequiv. H ⁺ /g	2.45	1.72
Catalytic activity in gaseous phase, % acetone ^b	10.1	14.8
Catalytic activity in liquid phase, % acetone ^b	3.2	4.1

^a The average values for all the prepared samples. ^b For details on testing the catalytic activity see the previous work¹.

TABLE II
Oxidation of organic compounds by molecular oxygen catalysed by polymers A and B

Starting compound	Oxidation product	Yield of the product, mol. %	
		catalyst A	catalyst B
Ethanol	acetaldehyde	0.32	0.61
1-Butanol	butyraldehyde	0.94	1.56
2-Butanol	methyl ethyl ketone	5.65	7.53
Cyclohexanol	cyclohexanone	5.80	6.36
Butyraldehyde	butyric acid	40.46	42.62
Isobutyraldehyde	isobutyric acid	49.51	53.95
Isovaleraldehyde	isovaleric acid	79.51	83.74
Benzaldehyde	benzoic acid	3.95	7.96

tion mixture, this indicates that the substance formed is also catalytically active. Experiment made in the absence of *p*-toluenesulphonic acid proved that the quinone dissolved in organic solvents or in water does not exhibit measurable catalytic effectiveness for the oxidation of 2-propanol. Its activity increases in the presence of the acid in the reaction medium, which results in its decomposition by the reaction with the acidic component. As illustrated in Fig. 1, the experiment made with nitrogen in place of oxygen shows that quinone itself is capable of converting 2-propanol into acetone, obviously *via* oxidative dehydrogenation. The amount of acetone so formed demonstrates, however, that only small portion of quinone (about 6–10%) reacts in this way, since during short period the quinone is completely converted by its reaction with *p*-toluenesulphonic acid into the product which is not obviously capable of transforming 2-propanol to acetone. In the presence of oxygen and the

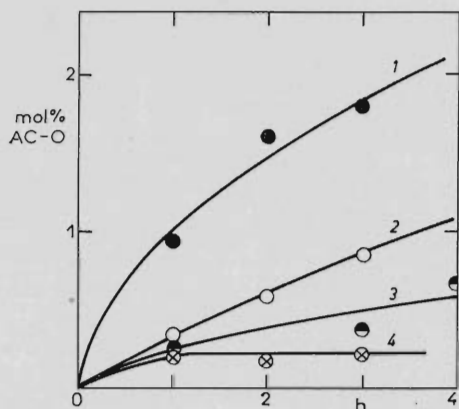


FIG. 1

Conversion curves for the catalytic liquid phase oxidation of 2-propanol by oxygen. 1 1.5 ml of 2-propanol, 0.1 g of the catalyst H., 0.2 ml of water, oxygen pressure 784 kPa, 2 2.5 ml of 2-propanol, 0.1 g of quinone, 1.5 ml of water, 0.1 g of *p*-toluenesulphonic acid, oxygen pressure 784 kPa, 3 2.5 ml of 2-propanol, 0.1 g of quinone, 0.1 g of *p*-toluenesulphonic acid, oxygen pressure 784 kPa, 4 see curve 2, the reaction was carried out in the absence of oxygen at the pressure of nitrogen equaling to 784 kPa

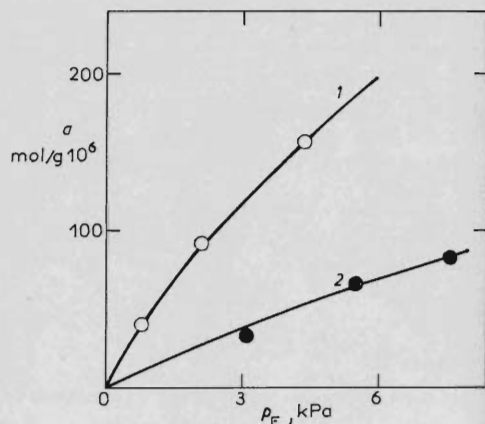


FIG. 2

Adsorption isotherms of oxygen on styrene-divinylbenzene copolymer with hydroquinone functional groups. *a* Sorbed amount of oxygen (mol/g catalyst), p_E the equilibrium pressure of oxygen at 120°C (kPa). 1 Polymer was converted into the reduced form by Ti(III) salt in aqueous medium. 2 Polymer was converted into the oxidized form by Fe(III) salt in aqueous medium

acid, however, quinone and the product of its reaction with the acid do catalyse the oxidation reaction. Experiments represented graphically in Fig. 1 demonstrate that the oxidation catalytic reaction is favourably affected by the presence of water in reaction medium.

In the case of the catalysts A and B we have also examined their thermal stability by the way reported in our previous work². The stability of carbon macromolecular skeleton of the catalysts prepared by the sulphonation at 180°C turned out to be identical with the stability of the catalysts reported earlier and prepared by sulphonation at 80–90°C (Fig. 1*a,b*, curves 1, 2 of the preceding publication²); it was further found that the stability of bonded sulphur is increased, since at 120°C and even at 150°C, the formation of sulphur dioxide does not take place. This fact can likely be linked to the substantially higher crosslinking of the polymer skeleton of the catalysts studied in this work. This crosslinking is realized both by carbon-carbon bonds and by sulphone bridges.

As the oxidation by molecular oxygen is always accompanied by the interaction of the oxygen with the catalyst, we made several measurements of the adsorption of oxygen at a temperature of 120°C. For this purpose we used the catalyst D (Table I of the preceding publication¹) which did not contain sulphonic acid groups and had the highest portion of quinone groups with respect to the undefined redox centres. This catalyst was converted first into the reduced form by treatment with the Ti(III) salt in water, followed by vacuum desorption to $1.3 \cdot 10^{-3}$ Pa for 6 h and by oxygen sorption from the pressure of *c.* 20 kPa up to the equilibrium. The sorption and desorption of oxygen could be repeated many times on one catalyst sample. It was found that the amount of oxygen sorbed equaled to $3.5 \cdot 10^{-5}$ mol O₂ per g of the catalyst. In further stage, the adsorption isotherms of oxygen were determined for the reduced and oxidized form of the same catalyst, the results being shown in Fig. 2. The sorption capacity of the reduced catalyst is more than two times greater compared to the oxidized catalyst, which means that we deal here with the chemical interaction of molecular oxygen with hydroquinone groups. This is in accordance with the results of our first work¹ in which the reduced form of these catalysts was converted by gaseous oxygen at elevated temperatures into the oxidized form, and the oxidation capacity was determined by titration in aqueous medium. It was further proved that under the same conditions, the sorption of oxygen does not take place on the starting chloromethylated styrene-divinylbenzene copolymers which do not exhibit redox capacity.

The activity of catalysts A and B was tested in the liquid phase under conditions used in the case of 2-propanol³ also for a series of organic compounds. The results of these experiments are presented in Table II; it is worth mentioning that oxidation of aldehydes produces in addition to the oxidation product also higher molecular compounds in considerable amounts, obviously as the results of the catalytic effect of acidic functional groups of the catalyst.

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